

Temperature Dependence of Hardness of Alumina-Based Ceramics

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Hardness was measured as a function of temperature (20° to 1000°C) for several Al₂O₃ ceramics, including single-crystal sapphire and polycrystalline aluminas containing different amounts of second phase. Hardness decreased steadily with increasing temperature for all materials tested, in accordance with a semi-empirical relation of the form $H = H_0 (1 - T/T_0)$. This behavior conformed with a thermally activated slip process, limited by Peierls stresses. At lower temperatures, the hardness values for debased aluminas were less (smaller H_0) than for the pure materials, consistent with a reduction in shear modulus resulting from the "soft" phase. However, at higher temperatures the hardness values for all the aluminas converged (identical T_0 , i.e., material-invariant activation energy). The latter behavior indicated that the temperature dependence of the indentation deformation was controlled predominantly by the Al₂O₃ component.

IN VIEW of the potential use of ceramics as high-temperature materials, it is perhaps remarkable that so little is known about their "hot hardness" properties. Studies by Westbrook,¹ Atkins and Tabor,² and Naylor and Page³ stand out as important, but isolated, contributions. Particularly surprising is the lack of attention in this respect paid to Al₂O₃, one of the most widely used of all ceramics. The data that do exist on this material^{1,4,5} show a general tendency for the hardness to decrease strongly with temperature, suggesting some activated process. However, there apparently has been no attempt to compare data for pure and debased aluminas, or even for single-crystal and polycrystal aluminas, to determine the influence of micro-

structure. Thus, the role of such factors as grain-boundary phase, so critical to creep properties, remains largely undetermined.

The present work investigates the temperature dependence of several Al₂O₃ ceramics, with the aim of examining the role of microstructural variables.

EXPERIMENTAL PROCEDURE

The materials tested included single-crystal sapphire and nominally pure and debased polycrystalline aluminas. Table I lists these materials, along with some of their essential properties. The second phase in the debased materials was determined by scanning and transmission

electron microscopy to be a partially crystallized aluminosilicate glass, concentrated primarily in pockets between the grains (Fig. 1).

Before hardness testing, each sample was mechanically polished to a 1-μm surface finish. Hot-hardness tests[†] were made at 10-N loads using a Vickers indenter at a constant penetration rate (300 μm/s) and fixed dwell time (15 s) at maximum load. Measurements were taken at 200°C intervals to 1000°C (homologous temperature $T/T_m \approx 0.55$) under 1 mPa (10⁻⁵ torr). Indentation half-diagonals were measured from optical and scanning electron micrographs and converted to hardness values using $H = P/2a^2$, with P the load and a the indentation half-diagonal. Mean and standard deviations were evaluated from five indentations per temperature setting per material.

RESULTS

Figure 2 plots hardness as a function of temperature for the different aluminas. The typical standard deviation for the points in this plot is ±5%, but error bars are omitted to avoid data overlap. The hardness for all materials decreases nearly linearly with temperature. For sapphire[§] and the nominally pure polycrystalline aluminas,^{††} the data are practically indistinguishable. This indicates that, for the range of temperatures studied, grain boundaries play no significant role in determining hardness. On the other hand, the data for the debased aluminas fall below those for the pure aluminas. This is not inconsistent with the expected role of a soft phase. However, the greatest differences in values occur at the lower tem-

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§Using Model No. QM, high-temperature microhardness tester, Instrument Div., Nikon, Inc., Garden City, NY.

¶Adolph Mellor Co., Providence, RI; surface orientation (2110).

†Vital, Coors Porcelain Co., Golden, CO.

**AD999, Coors Porcelain Co.

Table I. Properties of Materials Used in This Study

Material	Second phase (vol%)	Grain size (μm)	μ (GPa)	H_0 (GPa)
Sapphire*			174	23.2
Vital†	0.2	20	161	23.2
AD999†	0.2	3	158	23.2
AD96†	7	11	125	17.6
AD90†	18	4	113	15.8

*Adolph Mellor Co., Providence, RI; surface orientation (2110). †Coors Porcelain Co., Golden, CO.

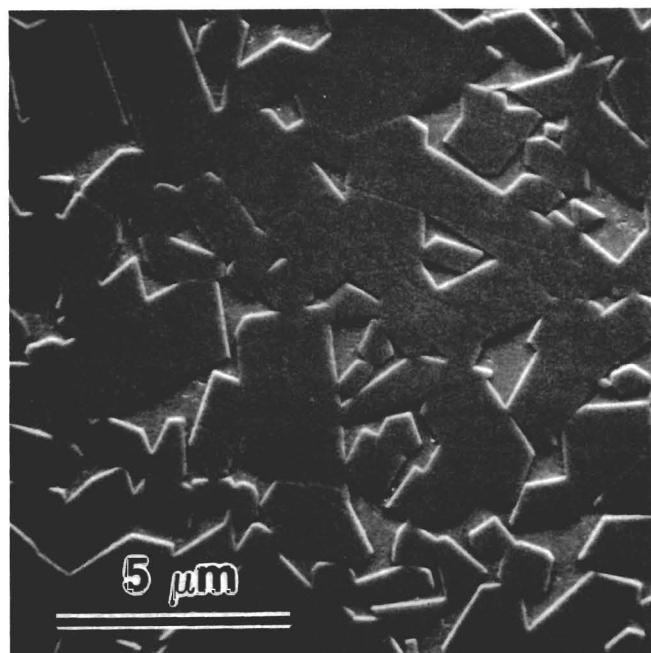


Fig. 1. SEM of polished section of debased (AD90) alumina, showing pockets of aluminosilicate glass phase between the Al₂O₃ grains. Note that the latter grains make close contact with adjacent neighbors; i.e., the Al₂O₃ structure is "connected."

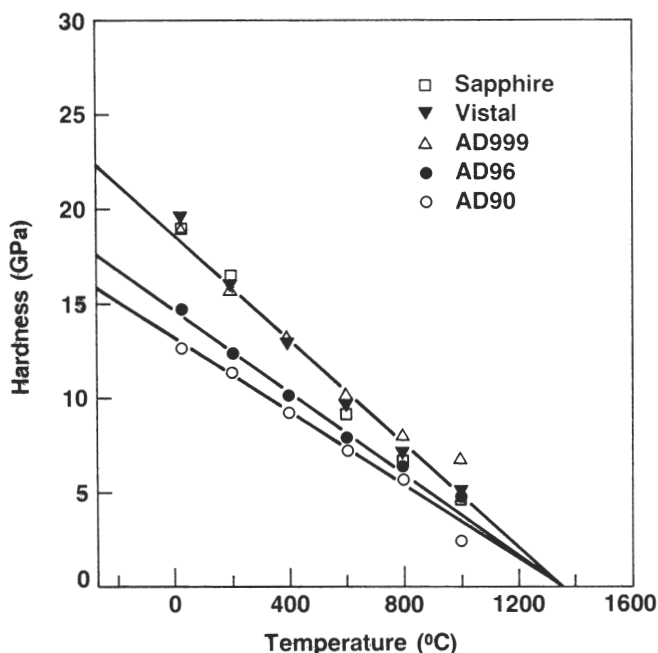


Fig. 2. Plot of hardness versus temperature for the alumina materials listed in Table I. Solid lines are linear fits to Eq. (2).

peratures: indeed, the data for all materials converge strongly at the upper end of the temperature scale.

The general implication of these qualitative observations is that the activation process for the deformation is controlled by the same, primary component in all the materials, i.e., the Al_2O_3 . Microscopic examination of the surface regions around the indentation sites revealed the extent and density of slip lines to be comparable in the sapphire and the relatively coarse-grained polycrystalline alumina⁴ at elevated temperatures (albeit confined within the grains in the latter material), suggesting that the availability of suitably oriented slip systems is no limiting factor in the deformation process.

HARDNESS AS A THERMALLY ACTIVATED SLIP PROCESS

With these features in mind, an attempt was made to reconcile the results with theoretical relations for dislocation-controlled strain rates. An earlier paper⁶ argued that dislocation slip processes account for the greater part of the hardness deformation in sapphire, even at room temperature (although the indentation shear stresses were close to the theoretical cohesive limit for the Al_2O_3 structure, and twinning was also active). More quantitative studies^{7,8} of the deformation processes in sapphire confirmed the activity of well-defined dislocation slip systems; moreover, the flow stresses for these systems follow the same precipitous decreases with

temperature that appear in Fig. 2. Accordingly, a semiempirical relation for dislocation velocities for activation over energy barriers⁹ yields

$$v = \beta b \nu \exp [-(\Delta F_0/kT)(1-\tau/Y)] \quad (1)$$

where β is a dimensionless constant, b is the Burgers vector, ν is a lattice vibration frequency, ΔF_0 is a zero-stress ($\tau=0$) activation energy for the dislocation motion, τ is the resolved shear stress on the relevant slip plane, Y is the theoretical shear strength of the crystal ($\propto \mu$, with μ the shear modulus), k is Boltzmann's constant, and T is absolute temperature. The barriers in Eq. (1) could be associated with either the intrinsic lattice resistance or extrinsic obstacles. The main feature of this equation is the appearance of a strong stress term in the activation exponent.

Consider the conditions under which the hardness tests were made. Recall that the indenter in the present experiments was loaded at a constant penetration rate, followed by a fixed dwell time. In the approximation that the bulk of the deformation occurred during the initial penetration stage (i.e., neglecting any additional deformation that might have occurred in the dwell time after achieving maximum load), the average steady-state shear-strain rate in the near-contact field was the same for all indentations, regardless of material or temperature. But for dislocation-controlled deformation, the steady-state shear rate is simply $\dot{\gamma} = \rho b v$, where ρ is the dislocation density. Surely, ρ will depend on the resolved shear stress, τ (notably at the higher temperatures), but such a dependence will appear only as a preexponential factor (usually power law⁹) in the shear-strain rate, and to a first approxima-

tion may be neglected compared to the exponential dependence in Eq. (1). With this qualification, ν is constant. Finally, the hardness, H , will scale directly with the resolved shear stress, τ . Then Eq. (1) may be rearranged to give

$$H = H_0(1 - T/T_0) \quad (2)$$

where $H_0 \propto Y \propto \mu$ is the hardness at 0 K and $T_0 \propto \Delta F_0$ is the "softening" temperature at which the hardness goes to zero.

The solid lines in Fig. 2 are fits of Eq. (2) to the data. In this fitting, no attempt is made to distinguish between the single-crystal and pure polycrystal forms of Al_2O_3 . However, separate lines are drawn through the data for two debased aluminas. All the data can be fitted to a common value of $T_0 = 1350$ K. The values of H_0 , however, differ for each curve. These values are included in Table I.

DISCUSSION

Can one attach any physical significance to the parameters obtained from the data fits? First, it should be emphasized that the "goodness" of fit obtained in Fig. 2 establishes consistency with, but not proof of, a flow process controlled by dislocation motion over lattice barriers. There are several variants of Eq. (1),⁹ along with the usual (empirical) Arrhenius function, and most of these fit equally well to the data.

The modeling indicates that the deformation is stress activated. Moreover, the apparent constancy in T_0 ($\propto \Delta F_0$) suggests that the activation energy is the same for all alumina materials, which in turn suggests that it may be slip in the hard, primary Al_2O_3 component that controls the activation process. This possibility differs somewhat from that advanced by Czernuszka and Page⁵ in an earlier hardness-temperature study of two debased aluminas, that suggested that the sharp falloff in hardness with increasing temperature might result in part from a softening of the second phase. However, those workers made no attempt to compare their results with controls containing no second phases. Also, the estimated softening temperature of the glass in the alumina materials used here,^{††,‡‡} $\approx 900^\circ\text{C}$ (from viscosity data for aluminosilicate glass¹⁰), suggests that the second phases may retain much of their load-bearing capacity at intermediate temperatures. Furthermore, it appears from Fig. 1 that, despite the presence of the glassy pockets, the Al_2O_3 grains in the debased structures maintain close contact with their neighbors; i.e., the alumina structure remains effectively "connected." In this latter context, the indentation field contains a large hydrostatic-stress component that would help to enhance such intergranular contact.

This picture of a connected alumina structure is also consistent with the "athermal" element of the hardness behavior. The shear modulus for such a

^{††}AD90, Coors Porcelain Co.

^{‡‡}AD96, Coors Porcelain Co.

structure would be expected to diminish systematically with increasing glass content, in accordance with some law of mixtures. The reduction in H_0 ($\propto \mu$) with increasing glass content (Table I) might thus be interpreted as a reduction in capacity for the structure to withstand shear loading; H_0 indeed appears to scale approximately with the measured shear modulus listed in Table I.

From these observations, soft phases (at least at the levels considered in the present work) may not always be unduly deleterious to the load-sustaining capacity of ceramics at moderate temperatures (to 1000°C), particularly if the loading has a large compressive component (e.g., as in the contact events responsible for erosion and wear). This insensitivity to composi-

tion directly contrasts to creep properties at higher temperatures.

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REFERENCES

- ¹J. H. Westbrook, "The Temperature Dependence of Hardness of Some Common Oxides," *Rev. Hautes Temp. Réfract.*, **3** [1] 47-57 (1966).
- ²A. G. Atkins and D. Tabor, "Hardness and Deformation Properties of Solids at Very High Temperatures," *Proc. R. Soc. London A.*, **292**, 441-58 (1966).
- ³M. G. S. Naylor and T. F. Page, "Microstructural Studies of the Temperature Dependence of Deformation Structures around Hardness Indentations in Ceramics," *J. Microsc. (London)*, **130** [6] 345-60 (1982).
- ⁴T. N. Loladze, G. V. Bokuchava, and G. E. Davidova; pp. 251-57 in *Science of Hardness Testing and its Applications*. Edited by J. H. Westbrook and H. Conrad. American Society for Metals, Metals Park, OH, 1973.
- ⁵J. T. Czernuszka and T. F. Page, "A Problem in Assessing the Wear Behavior of Ceramics: Load, Temperature, and Environmental Sensitivity of Indentation Hardness," *Proc. Br. Ceram. Soc.*, **34** [8] 145-56 (1984).
- ⁶H. M. Chan and B. R. Lawn, "Indentation Deformation and Fracture of Sapphire," *J. Am. Ceram. Soc.*, **71** [1] 29-35 (1988).
- ⁷A. H. Heuer, N. J. Tighe, and R. M. Cannon, "Plastic Deformation of Fine-Grained Alumina (Al_2O_3): II, Basal Slip and Nonaccommodated Grain-Boundary Sliding," *J. Am. Ceram. Soc.*, **63** [1-2] 53-58 (1980).
- ⁸R. M. Cannon, "Mechanical Properties of MgO and Al_2O_3 ," pp. 818-38 in *Advances in Ceramics*, Vol. 10, Structure and Properties of MgO and Al_2O_3 Ceramics. Edited by W. D. Kingery. American Ceramic Society, Columbus, OH, 1984.
- ⁹H. J. Frost and M. F. Ashby, *Deformation Mechanism Maps*; Ch. 2. Pergamon Press, Oxford, 1982.
- ¹⁰E. B. Shand; p. 247 in *Engineering Glass*, Modern Materials, Vol. 6. Academic Press, New York, 1968.